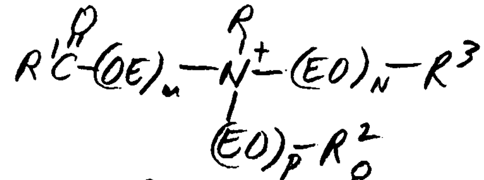
Silicates (+) ↑

FeO ↓ or BO₅ ↓ or $CaCO_3$ ↓

DERWENT-ACC-NO: 1997-386492

I 

R^2 may = R'C—

DERWENT-WEEK: 200524

TITLE: Flotation process for removing e.g. silicate(s) from ore - comprises passing air through ore suspension and removing impurities with foam, using special quaternised ester compounds as flotation collectors

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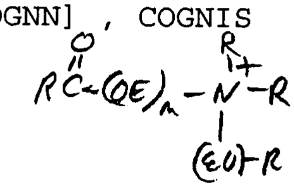
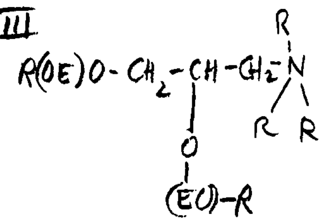
INVENTOR: DOBIAS, B; HEROLD, C ; KOPPL, D ; KOEPPL, D ; HEROLD, K

PATENT-ASSIGNEE: HENKEL KGAA[HENK] , COGNIS DEUT GMBH[COGNN] , COGNIS DEUT GMBH & CO KG[COGNN]

II 

PRIORITY-DATA: 1996DE-1002856 (January 26, 1996)

PATENT-FAMILY:

III 

PUB-NO	PUB-DATE	LANGUAGE	PAGES	MAIN-IPC
ES 2227665 T3	April 1, 2005	N/A	000	B03D 001/01
DE 19602856 A1	July 31, 1997	N/A	012	B03D 001/004
WO 9726995 A1	July 31, 1997	G	031	B03D 001/01
ZA 9700573 A	September 23, 1997	N/A	024	B03D 000/00
AU 9714431 A	August 20, 1997	N/A	000	B03D 001/01
EP 876222 A1	November 11, 1998	G	000	B03D 001/01
BR 9707082 A	April 13, 1999	N/A	000	B03D 001/01
AU 708335 B	August 5, 1999	N/A	000	B03D 001/01
MX 9805334 A1	October 1, 1998	N/A	000	B03D 001/01
EP 1025908 A1	August 9, 2000	G	000	B03D 001/01

KR 99067053 A	August 16, 1999	N/A	000	B03D 001/01
EP 1025908 B1	April 3, 2002	G	000	B03D 001/01
DE 59706919 G	May 8, 2002	N/A	000	B03D 001/01
ES 2174784 T3	November 16, 2002	N/A	000	B03D 001/01
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WO 9726995A1	N/A	1997WO-EP00186	January 17, 1997
ZA 9700573A	N/A	1997ZA-0000573	January 23, 1997
AU 9714431A	N/A	1997AU-0014431	January 17, 1997
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EP 876222A1	N/A	1997EP-0901048	January 17, 1997
EP 876222A1	N/A	1997WO-EP00186	January 17, 1997
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BR 9707082A	N/A	1997BR-0007082	January 17, 1997
BR 9707082A	N/A	1997WO-EP00186	January 17, 1997
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EP 1025908A1	Div ex	1997EP-0901048	January 17, 1997
EP 1025908A1	N/A	2000EP-0107539	January 17, 1997
EP 1025908A1	Div ex	EP 876222	N/A
KR 99067053A	N/A	1997WO-EP00186	January 17, 1997
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EP 1025908B1	Div ex	1997EP-0901048	January 17, 1997
EP 1025908B1	N/A	2000EP-0107539	January 17, 1997
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DE 59706919G	N/A	2000EP-0107539	January 17, 1997
DE 59706919G	Based on	EP 1025908	N/A
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ES 2174784T3	Based on	EP 1025908	N/A
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EP 876222B1	N/A	1997WO-EP00186	January 17, 1997
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ABSTRACTED-PUB-NO: DE 19602856A

BASIC-ABSTRACT:

The flotation process for removing mineral impurities, especially silicates, from ores comprises passing air through an aqueous suspension of the ground ore in the presence of a flotation aid and separating off the foam plus the impurities. The collector components used in the flotation aid comprise quaternised ester compounds (esterquats) of formula (I), (II) and/or (III), optionally with other anionic, cationic, amphoteric and/or non-ionic substances. In the formulae: R1CO, R5CO and R9CO = 6-24C acyl; R2, R3, R6 and R10 = H or 6-24C acyl; R4 = 1-4C alkyl or -(CH2CH2O)qH, where q = 1-12; R7, R8, R11, R12 and R13 = 1-4C alkyl; (m + n + p) or (m + n) = 0 or 1-12; and X = halide, alkylsulphate or alkylphosphate.

ADVANTAGE - The flotation aids have good biodegradability and high selectivity (especially for flotation of silicates), giving optimum foam thickness and half life even in the presence of high concentrations of magnesium.

ABSTRACTED-PUB-NO: EP 1025908B

EQUIVALENT-ABSTRACTS:

The flotation process for removing mineral impurities, especially silicates, from ores comprises passing air through an aqueous suspension of the ground ore in the presence of a flotation aid and separating off the foam plus the impurities. The collector components used in the flotation aid comprise quaternised ester compounds (esterquats) of formula (I), (II) and/or (III), optionally with other anionic, cationic, amphoteric and/or non-ionic substances. In the formulae: R1CO, R5CO and R9CO = 6-24C acyl; R2, R3, R6 and R10 = H or 6-24C acyl; R4 = 1-4C alkyl or -(CH2CH2O)qH, where q = 1-12; R7, R8, R11, R12 and R13 = 1-4C alkyl; (m + n + p) or (m + n) = 0 or 1-12; and X = halide, alkylsulphate or alkylphosphate.

ADVANTAGE - The flotation aids have good biodegradability and high selectivity (especially for flotation of silicates), giving optimum foam thickness and half life even in the presence of high concentrations of magnesium.

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DERWENT-CLASS: A25 A97 E19 J01 P41

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(56) Related Art
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(54) Title: BIODEGRADABLE QUATERNARY ESTERS USED AS FLOTATION AIDS

(54) Bezeichnung: BIOLOGISCH ABBAUBARE ESTERQUATS ALS FLOTATIONSHILFSMITTEL

(57) Abstract

The invention concerns the use of so-called quaternary esters as an aid for flotation of non-sulfidic minerals. It was discovered that the products of quaternary esterification of mono, di or trialkanolamine containing aliphatic carboxylic acids present good collector properties on the one hand, especially for the flotation of silicates, and on the other hand an exceptional biodegradability under both aerobic as well as anaerobic conditions.

(57) Zusammenfassung

Die Erfindung betrifft die Verwendung sogenannter Esterquats als Hilfsmittel bei der Flotation nichtsulfidischer Erze. Es wurde gefunden, daß die als Esterquats bezeichneten, quaternisierten Veresterungsprodukte der Mono-, Di- oder Trialkanolamine mit aliphatischen Carbonsäuren einerseits gute Sammlereigenschaften zeigen, insbesondere bei der Silikatflotation, andererseits sowohl unter aeroben wie auch unter anaeroben Bedingungen hervorragende biologische Abbaubarkeit gewährleisten.

Biologically Degradable Esterquats as Flotation Aids

Field of the Invention

This invention relates to so-called esterquats as aids in the flotation of nonsulfide ores. The quaternised esterification products of mono-, di- or trialkanolamines with aliphatic carboxylic acids, known as esterquats, show on the one hand good collector properties, especially in the flotation of silicates, and on the other hand excellent biological degradability both under aerobic and under anaerobic conditions.

Prior Art

Flotation is a generally used separation process for working up mineral raw materials in which valuable minerals are separated from worthless minerals. The nonsulfide minerals include, for example, apatite, calcite, fluorite, scheelite and other salt-like minerals, cassiterite, haematite, magnesite and other metal oxides, for example oxides of titanium and zirconium and also certain silicates and aluminosilicates.

Thus, **DE-A1 35 17 154**, for example, describes the use of surfactant mixtures as aids for the flotation of nonsulfide ores. In this case, mixtures of adducts of ethylene oxide and propylene oxide with a C_{8-22} fatty alcohol and at least one anionic, cationic or ampholytic surfactant are used. The use of quaternised ester compounds is neither mentioned nor inferred.

WO 94/26419 describes the flotation of silicate-containing calcite minerals. As a solution, the flotation process is carried out in the presence of a quaternary ammonium compound and an alkylene oxide adduct with an amino compound, the silicate collecting in the froth. The use of quaternised ester compounds in a corresponding flotation process is neither mentioned nor inferred.

DE-A1 41 06 866 discloses a process for the selective flotation of phosphorus minerals in which a mixture of salts of the semiesters of alkyl-substituted succinic acids and other anionic surfactants is used as collector.

DE-A1 41 05 384 also describes a process for the selective flotation of phosphorus minerals. According to this document, protein or peptide hydrolysates acylated with C_{6-24} carboxylic acids are added to the flotation pulp.

Calcite minerals are of considerable importance, for example in the paper industry. Calcite is an important filler in the paper industry with which inter alia the whiteness and transparency of the product can be regulated. Calcite minerals are often accompanied by silicates so that, to purify the calcite, the silicate - undesirable for many applications - has to be removed. Flotation is generally used for this purpose. Thus, calcite minerals can be freed from troublesome silicates, for example, by quaternary ammonium compounds in admixture with fatty alcohols or nonpolar hydrocarbons. However, the often very high demand for cleanly

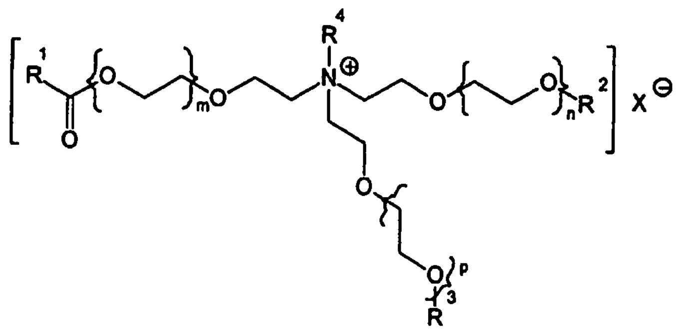
fractionated mineral constituents and hence flotation aids means that large quantities of wastewaters laden with auxiliaries have to be disposed of and thus normally enter the environment. Unfortunately, the quaternary ammonium compounds hitherto used for the flotation of silicates are distinguished by high ecotoxicity and by extremely unfavourable degradation behaviour so that they can be expected to accumulate in the environment and hence to cause long-term damage to sensitive ecosystems. Another disadvantage of hitherto known collectors is that minerals with a high magnesium content can only be floated with considerable difficulty, if at all. In conjunction with conventional collectors based on quaternary ammonium compounds, magnesium salts lead to an extremely stable froth which has a long half life (ie. collapses only slowly) and, hence, at least greatly delays separation of the floated material. Whereas a froth collapsing too quickly can generally be adjusted without difficulty to the required density and hence to the required half life by frothing agents, reducing the half life normally presents considerable problems. The conventional addition of defoamers, which are surface-active, generally modifies the interaction between collector and minerals in such a way that elaborate series of tests have to be carried out to establish the required balance between half life and the separation result. The present invention sought to remedy this situation.

Accordingly, the problem addressed by the present invention was to provide a biologically degradable flotation aid which, on the one hand, would guarantee high selectivity, especially in the flotation of silicates, but which on the other hand would show excellent biological degradability. In addition, the flotation aid according to the invention would even be able to be used in the flotation of minerals with a high magnesium content.

It has now surprisingly been found that quaternised ester compounds, so-called esterquats, show high silicate selectivity, are readily biodegradable and can be combined with various co-collectors and guarantee optimal froth density and half life, even in the flotation of high-magnesium minerals.

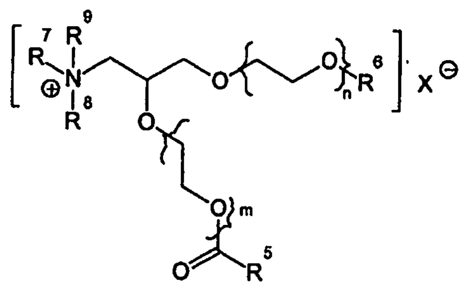
Description of the Invention

Accordingly, the present invention relates to a process for the removal of impurities, especially silicates, from ore mixtures by flotation in which ground ore mixture is mixed with water to form a suspension, air is introduced into the suspension in the presence of a flotation aid and the froth formed is removed together with the floated impurities present therein, characterised in that quaternised ester compounds (esterquats) corresponding to general formulae (I) or (II):



(I)

in which R^1CO is an acyl group containing 6 to 24 carbon atoms, R^2 and R^3 independently of one another represent hydrogen or have the same meaning as R^1CO, R^4 is an alkyl group containing 1 to 4 carbon atoms or a $(CH_2CH_2O)_qH$ group, m, n and p together stand for 0 or numbers of 1 to 12, q is a number of 1 to 12 and X is halide, alkyl sulfate or alkyl phosphate,



(II)

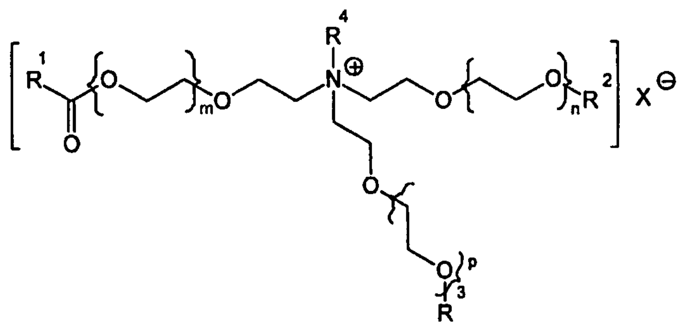
in which R^5CO is an acyl group containing 6 to 24 carbon atoms, R^6 has the same meaning as R^5CO, R^7, R^8 and R^9 independently of one another are alkyl groups containing 1 to 4 carbon atoms, m and n together stand for 0 or numbers of 1 to 12 and X is halide, alkyl sulfate or alkyl phosphate, are used individually or in admixture, optionally together with other anionic, cationic, amphoteric and/or nonionic substances, as the collector component.

Collectors in the context of the present invention are either the esterquats according to the invention or substances known to the expert as collectors by virtue of their effect. Mixtures of one or more collectors and optionally other additives, which are added to the collector(s) for example simply for their rheological effect or which otherwise promote the handling or processability of the collectors, are referred to hereinafter as flotation aids. Accordingly, they comprise the collector mixture and all other additives. However, this does not mean that collectors cannot also be used as the sole constituent of such a flotation aid providing the collector in question can be handled under the in-use conditions and can be used in the intended manner. Equally, there is nothing to stop individual components of the flotation aid as a whole from being separately introduced into the flotation machine.

"Esterquats" are generally understood to be quaternised fatty acid triethanolamine ester salts. They are known substances which may be obtained by

the relevant methods of preparative organic chemistry. Reference is made in this connection to International patent application **WO 91/01295** (Henkel), according to which triethanolamine is partly esterified with fatty acids in the presence of hypophosphorous acid, air is passed through and the resulting reaction mixture is quaternised with dimethyl sulfate or ethylene oxide. **US 3,915,867, US 4,370,272, EP-A2 0 239 910, EP-A2 0 293 955 A2, EP-A2 0 295 739** and **EP-A2 0 309 052 A2** are cited as representative of the extensive prior art available on the subject. Reviews on the same subject have been published, for example, by O. Ponsati in **C.R. CED Congress, Barcelona, 1992, page 167**, by R. Puchta et al. in **Tens. Surf. Det., 30, 186 (1993)**, by M. Brock in **Tens. Surf. Det. 30, 394 (1993)** and by R. Lagerman et al. in **J. Am. Oil Chem. Soc., 71, 97 (1994)**.

The quaternised fatty acid triethanolamine ester salts correspond to formula (I):



(I)

in which R^1CO is an acyl group containing 6 to 24 carbon atoms, R^2 and R^3 independently of one another represent hydrogen or have the same meaning as R^1CO, R^4 is an alkyl group containing 1 to 4 carbon atoms or a $(CH_2CH_2O)_qH$ group, m, n and p together stand for 0 or numbers of 1 to 12, q is a number of 1 to 12 and X is halide, alkyl sulfate or alkyl phosphate.

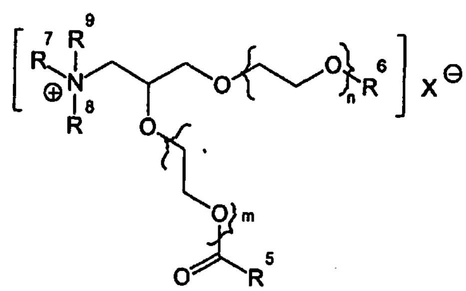
Typical examples of esterquats which may be used for the purposes of the invention are products based on caproic acid, caprylic acid, capric acid, lauric acid, myristic acid, palmitic acid, isostearic acid, stearic acid, oleic acid, elaidic acid, arachic acid, behenic acid and erucic acid and the technical mixtures thereof obtained, for example, in the pressure hydrolysis of natural fats and oils. Technical $C_{12/18}$ cocofatty acids and, in particular, partly hydrogenated $C_{16/18}$ tallow or palm oil fatty acids, tall oil fatty acid and partly hydrogenated tall oil fatty acid and also $C_{16/18}$ fatty acid cuts rich in elaidic acid are preferably used.

For the production of the quaternised esters, the fatty acids and the triethanolamine may be used in a molar ratio of 1.1:1 to 3:1. With the performance properties of the esterquats in mind, a ratio of 1.2:1 to 2.2:1 and preferably 1.5:1 to 1.9:1 has proved to be particularly advantageous. The preferred esterquats are technical mixtures of mono-, di- and triesters with an average degree of

esterification of 1.5 to 1.9, for example 1.64 to 1.9, and are derived from technical $C_{16/18}$ tallow or palm oil fatty acid (iodine value 0 to 40).

From the point of view of performance, quaternised fatty acid triethanolamine ester salts corresponding to formula (I), in which R^1CO is an acyl group containing 16 to 18 carbon atoms, more particularly acyl groups from partly hydrogenated technical $C_{16/18}$ tallow or palm oil fatty acid cuts (iodine value 0 to 40), R^2 has the same meaning as R^1CO, R^3 is hydrogen, R^4 is a methyl group, m, n and p stand for 0 and X is methyl sulfate, have proved to be particularly advantageous in the flotation of silicates.

In addition to quaternised fatty acid triethanolamine ester salts, other suitable esterquats are quaternised ester salts of fatty acids with 1,2-dihydroxypropyl dialkylamines corresponding to formula (II):



(II)

in which R^5CO is an acyl group containing 6 to 24 carbon atoms, R^6 has the same meaning as R^5CO, R^7, R^8 and R^9 independently of one another are alkyl groups containing 1 to 4 carbon atoms, m and n together stand for 0 or numbers of 1 to 12 and X is halide, alkyl sulfate or alkyl phosphate.

Floatable minerals may be divided into the two groups of polar and nonpolar minerals, the surface of nonpolar minerals being difficult to hydrate so that minerals such as these ultimately have to be classified as hydrophobic. Examples of nonpolar minerals are graphite, sulfur, molybdenite, diamond, coal and talcum which are all floatable in their naturally occurring state. Normally, the ores containing these minerals merely require the addition of nonspecific collectors, for example diesel oil, kerosene or similar hydrocarbons, such as oxo oils, to support the natural hydrophobicity of the minerals.

By contrast, polar minerals have strong covalent or ionic surface bonds which are accessible to rapid hydration by water molecules in the form of multilayers. These minerals include, for example, malachite, azurite, chrysocolla, wulfenite, cerrusite, witherite, magnesite, dolomite, smithsonite. rhodochrosite, siderite, magnetite, monazite, haematite, goethite, chromite, pyrolusite, borax, wolframite, columbite, tantalite, rutile, zircon, hemimorphite, beryl and garnet.

The sulfide minerals are an exception. In their case, collectors which are capable of reacting with the sulfide groups present at the surface of the mineral, for example xanthates, dithiophosphates, mercaptans, thiocarbamates or dithiolates, are used almost without exception, the formation of nascent bubbles generally becoming the dominant flotation mechanism.

Typical steps in the process sequence are generally first the dry or preferably wet grinding of the minerals, suspension of the resulting ground mineral in water in the presence of the flotation aid and, preferably after a contact time of the collectors and optionally co-collectors present in the flotation aid to be determined in each individual case, injection of air into the suspension to produce the flotation froth.

The flotation behaviour of the individual mineral constituents can be controlled within certain limits through the particle size distribution of the ground mineral. Conversely, however, the use of the collector is also influenced by the particle size so that both particle size and, for example, collector concentration may be determined in situ in a brief series of tests. Generally, however, it may be said that the particles have to be increasingly hydrophobicised with increasing particle size before flotation occurs. As a general rule, the ores should be so finely ground that the individual fine particles consist only of one type of mineral, namely either the valuable minerals or the impurities. The ideal particle size normally has to be determined in dependence upon the particular mineral. In the present case, however, a particle size distribution of around 5 to 500µm has generally been found to be practicable, narrower distributions being of advantage in some cases. For example, silicate-rich ores can be separated by flotation with excellent results using the flotation aids according to the invention providing less than 40% by weight, preferably less than 30% by weight and more preferably less than 15% by weight of the total ore fraction has particle sizes of less than 250µm. To enable the flotation process to be optimally carried out, it can be particularly preferred for the particles larger than 125µm in size to make up less than 15% by weight or preferably less than 10% by weight or even 6% by weight. The lower limit to the particle sizes is determined both by the possibility of size reduction by machine and also by the handling properties of the constituents removed by flotation. In general, more than 20% by weight of the ground mineral should be smaller than about 50µm in size, a percentage of particles with this diameter of more than 30 or even 40% by weight, for example, being preferred. According to the invention, it is of particular advantage for more than 40% by weight of the ore particles to be smaller than 45µm in diameter.

In certain cases, it may be necessary and appropriate to divide the ground mineral into two or more fractions, for example three, four or five fractions differing in their particle diameter and separately to subject these fractions to separation by flotation. According to the invention, the flotation aids according to the invention

may be used in only one separation step although, basically, they may even be used in several separation steps or in all necessary separation steps. The invention also encompasses the successive addition of several different flotation aids, in which case at least one or even more of the flotation aids must correspond to the invention. The fractions obtainable in this way may be further processed either together or even separately after the flotation process.

The technical parameters of the flotation plant in conjunction with a certain flotation aid and a certain ore can influence the result of the flotation process within certain limits. For example, it can be of advantage to remove the froth formed after only a short flotation time because the content of floated impurities or floated ore can change according to the flotation time. In this case, a relatively long flotation time can lead to a poorer result than a relatively short flotation time. Similarly, it can happen in the opposite case that the separation process leads to greater purity or otherwise improved quality of the valuable-mineral fraction with increasing time. Optimising external parameters such as these is among the routine activities of the expert familiar with the technical specifications of the particular flotation machine.

Reagents which modify surface tension or surface chemistry are generally used for flotation. They are normally classified as collectors, frothers, controllers, activators and depressants (deactivators).

Collectors are reagents which form a coating over the surface of the mineral and make it water-repellent and hence accessible to the adhesion of air bubbles. Nonsulfide minerals are generally floated with such collectors as, for example, fatty acids, amines, quaternary ammonium compounds, sulfonates and/or hydrocarbons. Known anionic collectors are, for example, saturated and unsaturated fatty acids, more particularly tall oil fatty acids, oleic acid, alkyl sulfates, more particularly alkyl sulfates derived from fatty alcohols and/or fatty alcohol mixtures, alkylaryl sulfonates, alkyl sulfosuccinates, alkyl sulfosuccinamates and acyl lactates. Known cationic collectors are, for example, primary aliphatic amines, more particularly the fatty amines emanating from the fatty acids of vegetable and animal fats, and certain alkyl-substituted and hydroxyalkyl-substituted alkylenediamines and water-soluble salts of these amines.

The esterquats are normally used either as sole collector component or as part of a mixture of several collectors and co-collectors in a quantity of 10 to 2000g/t of ore. Esterquats corresponding to general formula (I) are preferably used for the purposes of the invention.

So far as the choice of the preferred fatty acids and the optimal degree of esterification is concerned, the examples mentioned in respect of (I) also apply to the esterquats corresponding to formulae (II) and (III). The esterquats are normally marketed in the form of 50 to 90% by weight alcoholic solutions which, in general, may readily be diluted with water as required.

Quaternary ammonium compounds, such as cetyl trimethyl ammonium bromide or distearyl dimethyl ammonium chloride, do not count as biologically degradable under the OECD guidelines because no degradation occurs in particular under aerobic conditions. In sewage treatment plants, they are generally adsorbed onto the sludge and, hence, prevented from degrading any further. However, esterquats meet all the requirements which a flotation aid is expected to satisfy in regard to biological degradability. Thus, in the Closed Bottle Test (OECD Test No. 301 D), for example, esterquats are classified as readily biodegradable, ie. >80% BOD/COD. Additional C^{14} screening tests also confirm the complete degradation of esterquats. Esterquats occupy a prominent position among quaternary nitrogen compounds by virtue in particular of their biological degradability under aerobic and anaerobic conditions.

The esterquats may be used for the purposes of the invention either on their own or in admixture with other cationic, nonionic or - with certain provisos - even anionic surfactants as co-collectors.

It is of course important in this regard to ensure that the biological degradability of the collector/co-collector system is not affected by the addition of non-degradable or non-readily degradable co-collectors. Depending on the particular application and economic needs, the co-collectors may even be used in larger quantities than the esterquats, for example in a quantity of 80, 70 or 60% by weight. Normally, however, the co-collectors should only be used in small quantities together with the esterquats if they themselves are not readily biodegradable. In general, a quantity to which the upper limit is at around 50% by weight of the collector system as a whole should not be exceeded whereas smaller quantities of 40, 30 or 20% by weight can afford clear advantages in regard to biological degradability. This corresponds to collector/co-collector ratios of, for example, from about 0.95:1, 1:1, 1.1:1, 1.2:1, 1.3:1 or 1.4:1 to 2:1, 3:1 or 4:1. It may even be such that 10% by weight or less is sufficient for adequately optimising the collector properties of the system used so that 5, 3 or even 2% by weight and less of co-collector is sufficient. In overall terms, however, the biological degradability of the system as a whole is always improved by the addition of the esterquats according to the invention as collectors.

Cationic surfactants suitable for use as co-collectors include in particular amino compounds such as, for example, the acid addition salts of primary aliphatic amines and alkylenediamines substituted by α-branched alkyl groups or hydroxyalkyl-substituted alkylenediamines. Ether amines, ether diamines and fatty acid amido amines, for example the condensates of polyamines with fatty acids, are also suitable. Above all, the C_{8-24} fatty amines emanating from the fatty acids of native fats and oils are suitable as primary aliphatic amines. In their case, mixtures of fatty amines, for example tallow amines or hydrotallow amines obtainable from

the tallow fatty acids or hydrogenated tallow fatty acids via the corresponding nitriles and hydrogenation thereof, are generally used.

The amino compounds are generally used as such or as an acid addition compound in the form of a water-soluble salt. The salts are obtained by neutralisation which may be carried out both with equimolar quantities and with less than the equimolar quantity of acids. Suitable acids are, for example, sulfuric acid, phosphoric acid, hydrochloric acid, acetic acid and formic acid. Particularly good results in the flotation of silicates are obtained by using esterquats in conjunction with fatty acid hydroxyethyl imidazolines and/or fatty acid aminoethyl imidazolines and/or fatty acid aminoethanolamides and/or fatty acyl amidofatty acid imidazolinium salts and/or carboxylic acid amidoalkylamines.

An important class of cationic compounds are the quaternary ammonium compounds. Accordingly, the esterquats are preferably used together with quaternary ammonium compounds corresponding to formula (III):

$$\left[R^{10}-\overset{\displaystyle R^{11}}{\underset{\displaystyle R^{12}}{\overset{|}{\underset{|}{N^{\oplus}}}}}-R^{13} \right] X^{\ominus} \qquad \text{(III)}$$

in which R^{10}, R^{11}, R^{12} and R^{13} are linear and/or branched alkyl and/or alkenyl groups containing 1 to 24 carbon atoms, in a ratio of 0.01:1 to 100:1. For example, trimethyl alkyl (tallow) ammonium chloride (R^{10}, R^{11}, R^{12} = methyl, R^{13} = C chain distribution of the tallow fatty acids) or dimethyl dicocoalkyl ammonium chloride (R^{10}, R^{11} = methyl; R^{12}, R^{13} = C chain distribution of the cocofatty acids) is preferably added. These are mixtures of compounds corresponding to formula (III) obtainable in the working-up of fatty acid cuts, for example tallow fatty acid or cocofatty acid, and subsequent reaction to the corresponding quaternary ammonium compound.

The ampholytic surfactants suitable for use as co-collectors are compounds which contain at least one anionic group and one cationic group in the molecule, the anionic group preferably consisting of sulfonic acid or carboxyl groups and the cationic group preferably consisting of amino groups, preferably secondary or tertiary amino groups. Particularly suitable ampholytic surfactants are sarcosinates, taurides, N-substituted aminopropionic acids, alkylamidobetaines, imidazolinium betaines, sulfobetaines and succinamates.

Anionic surfactants may be used in accordance with the invention when no flocculation occurs between the esterquats and the corresponding anionic surfactant. This is generally the case when the esterquats bear one or more alkoxy groups, more particularly ethoxy groups. The production of such ethoxylated esterquats is described, for example, in **DE-A1 42 24 714**. Accordingly, these esterquats may be combined, for example, with alkyl benzene sulfonates, alkane

sulfonates, glycerol ether sulfonates, α-methyl ester sulfonates, sulfofatty acids, alkyl sulfates, fatty alcohol ether sulfates, glycerol ether sulfates, hydroxy mixed ether sulfates, monoglyceride (ether) sulfates, fatty acid amide (ether) sulfates, sulfosuccinates, sulfosuccinamates, sulfotriglycerides, ether carboxylic acids, alkyl oligoglucoside sulfates, alkyl (ether) phosphates and protein fatty acid condensates.

Nonionic surfactants may also be used in addition to the esterquats. Nonionic surfactants include in particular fatty alcohol polyglycol ethers, fatty amine polyglycol ethers, fatty acid amide polyglycol ethers, fatty acid polyglycol esters, alkoxylated triglycerides, alkyl oligoglycosides, sugar esters, sorbitan esters, polysorbates, polyol fatty acid esters, amine oxides, fatty acid alkanolamides, alkyl lactams, fatty acid-N-alkyl glucamides. The adducts of n moles of ethylene oxide and n moles of propylene oxide with C_{8-22} fatty alcohols (m and n each being numbers of 0 to 15) may be used in particular.

For example, ores of which the individual components have hitherto necessitated the separate use of cationic and anionic collectors in successive steps may optionally be separated in a single step by the collectors according to the invention so that both time and material can be saved. Such collective separation may be used, for example, to remove silicate and phosphate from iron ore.

The esterquats may also be used with advantage in conjunction with fatty alcohols. Fatty alcohols are compounds corresponding to formula (V):

$$R^{14}OH \qquad (V)$$

in which R^{14} is an aliphatic, linear or branched hydrocarbon radical containing 6 to 24 carbon atoms and 0 and/or 1, 2 or 3 double bonds. The fatty alcohols may be used together with the esterquats and optionally together with other co-collectors in a ratio of 0.1:1 to 10:1. It is preferred to use C_{6-8} fatty alcohols which may optionally be employed as diluents for the collectors according to the invention and at the same time as frothers. Particularly suitable C_{6-8} fatty alcohols are isotridecanol and 2-ethyl hexanol.

The formation of froth may be supported by the use of so-called frothing agents which guarantee collectors with an inadequate tendency to froth a sufficiently high froth density and a sufficiently long froth life to enable the laden froth to be completely removed. In general, the use of the collectors or collector/co-collector systems mentioned above will eliminate the need to use other frothers. In special cases, however, it may be necessary - depending on the flotation process used - to regulate the frothing behaviour. In this case, suitable frothers are, for example, alcohols, more particularly aliphatic C_{5-8} alcohols such as, for example, n-pentanol, isoamyl alcohol, hexanol, heptanol, methyl isobutyl carbinol, capryl alcohol, 4-heptanol, which all have good frothing properties. Natural oils may also be used to support frothing. In particular, alcohols, ethers and ketones, for example α-terpineol, borneol, fennel alcohol, piperitone, camphor, fenchol or 1,8-cineol, have

both a collecting effect and a frothing effect. Other suitable frothers are the polypropylene glycol ethers mentioned in the list of nonionic collectors.

The flotation aids according to the invention may also contain other substances, for example, depressants, activators, pH regulators and dispersants.

Depressants which may be effectively used for the purposes of the invention include, for example, naturally occurring polysaccharides, such as guar, starch and cellulose. Quebracho, tannin, dextrin (white dextrin, British gum, yellow dextrin) and other chemical derivatives may also be used, including in particular the derivatives of starch, guar and cellulose molecules of which the hydroxyl groups may be equipped with a broad range of anionic, cationic and nonionic functions. Typical anionic derivatives are carboxylates, sulfates, sulfonates, xanthates, phosphates. Typical cationic derivatives are epoxypropyl trimethyl ammonium salts while methyl, hydroxyethyl and hydroxypropyl derivatives are mainly used as nonionic compounds.

In one preferred embodiment, the esterquats are used in the flotation of silicates. Accordingly, the present invention also relates to flotation aids containing the esterquats of formulae (I) or (II) defined above. In particular, the flotation aids according to the invention contain the esterquats and also fatty alcohols and/or quaternary ammonium compounds corresponding to formula (III). To adjust their rheological behaviour, the flotation aids according to the invention may contain solvents in a quantity of 0.1 to 40% by weight, preferably in a quantity of 1 to 30% by weight and more preferably in a quantity of 2 to 15% by weight.

Suitable solvents are both the $C_{5\text{-}8}$ alcohols mentioned elsewhere and other alcohols with a shorter chain length. Thus, the flotation aids according to the invention may contain small quantities of glycols, for example ethylene glycol, propylene glycol or butylene glycol, and also monohydric linear or branched alcohols, for example ethanol, n-propanol or isopropanol.

Examples

The following Examples illustrate the effectiveness of the collectors according to the invention on the one hand in the flotation of silicate-containing ores and, on the other hand, in flotation with high magnesium concentrations.

Table 1 shows the results obtained with various flotation aids containing at least one collector according to the invention. Table 2 shows the effectiveness of various types of collectors - both conventional and corresponding to the invention - under conditions of high magnesium concentrations.

OMC 6317	= Frother (Henkel)
OMC 6024	= Frother (Henkel)
AU 46	= Biodegradable esterquat (Henkel)
AU 56	= Biodegradable esterquat (Henkel)

DKMA = Dicocoalkyl dimethyl ammonium chloride
TTAC = Trimethyl tallow ammonium chloride
OMC 5044 = Cationic collector (Henkel)
A = Yield AG = Feed
F = Floated material conc. = Rest
Particle size distribution: >40μm: >50% by weight
Silicates: about 1.5 to 2.5% by weight
Calcite: about 97.5 to 98.5% by weight

Table 1

Effectiveness of the Collectors According to the Invention in Various Flotation Aids

Sample No.	Reagents in g/t	Yield F in g	Yield conc. in g	AG:HCl-insol. in %	F: HCl-insol. in %	Conc.: HCl-insol. in %	Calcite Loss in %
1	OMC 6317=100 AU 46=660	39.8	383	2.6	25.68	0.09	7.19
2	OMC 6317=100 AU 46=560	75.4	361.5	2.6	13.56	0.18	15.31
3	OMC 6317=85 AU 46=320	59.7	438	2.2	18.4	0.57	10.04
4	OMC 6024=85 AU46+OMC5044 1:1=559.7	50.2	521.5	2.5	23.9	0.13	6.82
5	OMC6024=75.5 OMC 5044/AU 46 1:1 = 301.8	45.8	749.2	2.5	37.2	0.06	3.69

Table 2

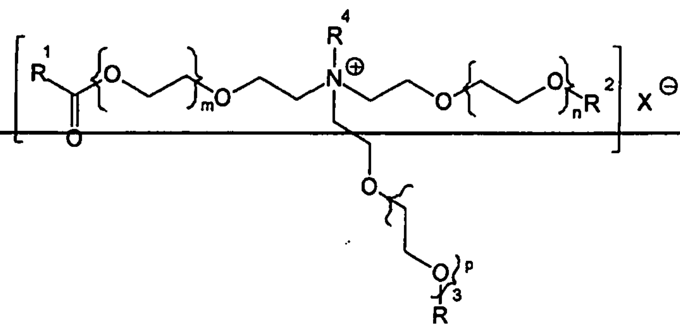
Effectiveness of Various Collectors at High Magnesium Concentrations

Product	AS %	Addition of AS	Quantity Product g	Test Solution	Foam Height (ml)	Half Life mins. (dec.)
AU 46	90	1%	2.26 2.29	2% $MgCl_2$ Solution 2% $MgCl_2$ Solution	220 220	2:35 (2.58) 2:35 (2.58)
AU 36	85	1%	2.38 2.45	2% $MgCl_2$ Solution 2% $MgCl_2$ Solution	220 220	3:40 (3.67) 3:40 (3.67)
DKMA	77	1%	2.6 2.6	2% $MgCl_2$ Solution 2% $MgCl_2$ Solution	220 220	Foam stable Foam stable
TTAC	52	1%	3.85 3.85	2% $MgCl_2$ Solution 2% $MgCl_2$ Solution	840 850	6:10 (6.17) 6:10 (6.17)
AU 46	90	1%	2.27 2.54	5% $MgCl_2$ Solution 5% $MgCl_2$ Solution	220 220	0:30 (0.5) 0:30 (0.5)
AU 36	85	1%	2.37 2.39	5% $MgCl_2$ Solution 5% $MgCl_2$ Solution	220 220	0:20 (0.33) 0:20 (0.33)
DKMA	77	1%	2.6	5% $MgCl_2$ Solution	220	Foam stable
TTAC	52	1%	3.85 3.85	5% $MgCl_2$ Solution 5% $MgCl_2$ Solution	820 820	7:20 (7.33) 7:20 (7.33)

Table 2 shows that only the collectors according to the invention lead to readily collapsing foams with short half lives which are desirable in the flotation of ores.

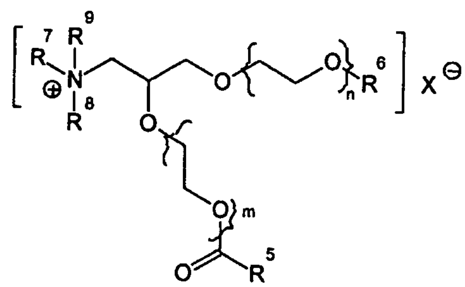
The claims defining the invention are as follows:

1. A process for the removal of impurities, from ore mixtures by flotation in which ground ore mixture is mixed with water to form a suspension, air is introduced into the suspension in the presence of a flotation aid and the froth formed is removed together with the floated impurities present therein, characterised in that quaternised ester compounds ("esterquats") corresponding to general formulae (I) or (II):



(I)

in which R^1CO is an acyl group containing 6 to 24 carbon atoms, R^2 and R^3 independently of one another represent hydrogen or have the same meaning as R^1CO, R^4 is an alkyl group containing 1 to 4 carbon atoms or a $(CH_2CH_2O)_qH$ group, m, n and p together stand for 0 or numbers of 1 to 12, q is a number of 1 to 12 and X is halide, alkyl sulfate or alkyl phosphate,



(II)

in which R^5CO is an acyl group containing 6 to 24 carbon atoms, R^6 has the same meaning as R^5CO, R^7, R^8 and R^9 independently of one another are alkyl groups containing 1 to 4 carbon atoms, m and n together stand for 0 or numbers of 1 to 12 and X is halide, alkyl sulfate or alkyl phosphate, are used individually or in admixture, optionally together with other anionic, cationic, amphoteric and/or nonionic substances, as the collector component.

2. The process as claimed in claim 1 whereby in formula (1):

R^1CO is an acyl group containing 6 to 24 carbon atoms;

R^2 represents R^1CO;

R^3 represents R^1CO or hydrogen;

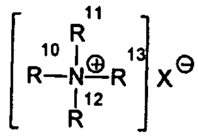
R^4 is an alkyl group containing 1 to 4 carbon atoms or a $(CH_2CH_2O)_qH$ group;

m, n and p together stand for 0 or numbers of 1 to 12;

q is a number of 1 to 12;

X is a halide, alkyl sulfate or alkyl phosphate.

3. A process as claimed in claim 1 or claim 2, characterised in that esterquats corresponding to formulae (I) and/or (II) are used together with quaternary ammonium compounds ("QUATS") corresponding to formula (III):



(III)

in which R^{10}, R^{11}, R^{12} and R^{13} are linear and/or branched alkyl and/or alkenyl groups containing 1 to 24 carbon atoms, in a ratio of esterquat to QUAT of 0.01:1 to 100:1.

4. A process as claimed in any one of claims 1 to 3, characterised in that the esterquats are used together with fatty alcohols containing an aliphatic linear or branched hydrocarbon radical with 6 to 24 carbon atoms and 0 and/or 1, 2 or 3 double bonds in a ratio of esterquat to fatty alcohol of 0.1:1 to 10:1.

5. A process as claimed in any one of claims 1 to 4, characterised in that the esterquats are used together with fatty acid hydroxyethyl imidazolines and/or fatty acid aminoethyl imidazolines and/or fatty acyl amidofatty acid imidazolinium salts and/or fatty acid aminoethyl ethanolamides and/or carboxylic acid amidoalkylamines.

6. A process as claimed in any one of claims 1 to 5, characterised in that the esterquats are present in the mixtures used as flotation aids in a quantity of 50 to 99.9% by weight.

7. A process as claimed in any one of claims 1 to 6, characterised in that the collectors are used in a quantity of 10 to 2000g/t of ore.

8. A process as claimed in any one of claims 1 to 7, characterised in that the impurities are silicates.

9. A process for the removal of impurities, from ore mixtures by flotation in which ground ore mixture is mixed with water to form a suspension, air is introduced into the suspension in the presence of a flotation aid and the froth formed is removed together with the floated impurities present therein, substantially as hereinbefore described with reference to any one of the examples.

10. Ore mixtures from which impurities have been removed by a process as claimed in any one of claims 1 to 9.

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